



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number:

0 534 092 A1

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 92112943.3

⑮ Int. Cl. 5: B29C 67/14, B29B 15/08

⑭ Date of filing: 29.07.92

⑯ Priority: 31.07.91 US 739115

⑰ Date of publication of application:
31.03.93 Bulletin 93/13

⑱ Designated Contracting States:
CH DE ES FR GB IT LI SE

⑲ Applicant: HERCULES INCORPORATED
Hercules Plaza
Wilmington Delaware 19894-0001(US)

⑳ Inventor: Boll, David J.
4562 Jarrah Street
Salt Lake City, Utah 84107(US)
Inventor: Lowe, Kenneth A.

5936 W. Zina Circle
West Valley City, Utah 84120(US)

Inventor: McCarvill, William T.

3363 Norwood Road

Salt Lake City, Utah 84121(US)

Inventor: McCloy, Michael R.

6376 S. Westridge

Murray, Utah 84107(US)

⑳ Representative: Alber, Norbert et al
Patent- und Rechtsanwälte-Hansmann,
Vogeser, Boecker, Alber,
Albert-Rosshaupter-Strasse 65
W-8000 München 70 (DE)

㉓ Cure-on-the-fly system.

㉔ Fiber laminations with a resin therein are advanced to substantial cure in situ while resin impregnated fiber (in the form of individual tows, a band thereof, or a tape) is being placed on a workpiece on the mandrel by preheating the fiber in a temperature range of 100-700 °F for partially advancing the cure of the resin in the fiber, shaping the fiber to the desired shape, and laying up the partially advanced fiber on the workpiece on the mandrel while simultaneously nip point heating the fiber in an area proximate to the point where the fiber is being placed on the workpiece. A plurality of parameters are monitored during this placement in order to control the nip point heating so that the resin in the fiber is substantially cured while the fiber is being placed on the workpiece.

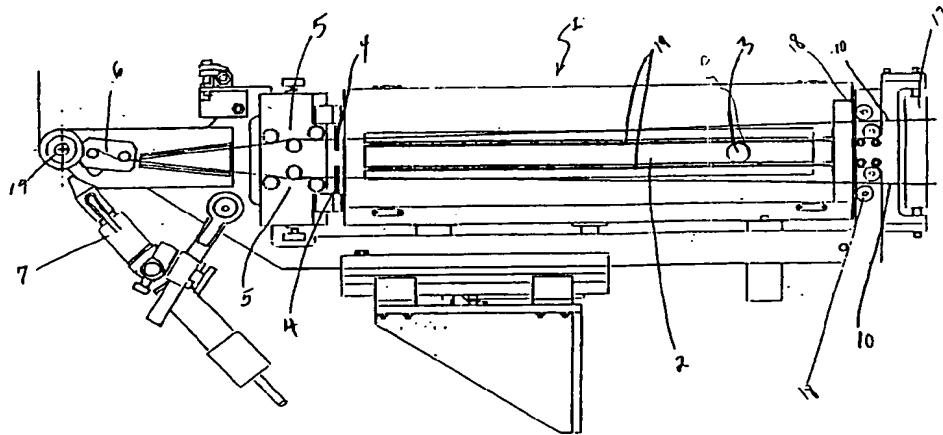


FIGURE 1

EP 0 534 092 A1

The present invention relates to composite structures manufacturing methods and apparatus for practicing such methods and, more particularly, to manufacturing composite structures using preimpregnated fibrous materials in fiber placement and/or tape laying systems.

Prior to the present invention, fiber placement systems generally consisted of placing rovings or tows 5 impregnated with either thermoplastic or thermosetting type resin as a single tow or an entire band of tows in a number of superimposed layers onto a workpiece on a mandrel to produce a geodesic shaped article. This geodesic shaped article was then placed in a bag, a vacuum was then created in the bag, and the bag was placed in an autoclave and heated at high temperatures and pressures in order to cure and consolidate the article.

10 Another technique used in the art to cure and consolidate composite structures uses only an oven rather than an autoclave. Autoclave curing requires constant monitoring and additional safety precautions as well as being more expensive in operation while oven curing does not require constant monitoring or additional safety precautions and is relatively inexpensive to operate. This technique places fiber tows using a wet filament winding technique where the composite material would gel at room temperature and then the 15 component part is cured in an oven.

These previous techniques produced parts that had high void levels (i.e., up to 10%) when oven cured, or required additional handling to produce low void levels parts (i.e., less than 2%). In the wet winding technique, an excess of resin had to be used, followed by a squeegee technique, or vacuum consolidation and gas removal during the oven cure to produce a low void part.

20 Both of the prior art fiber placement and wet winding processes have disadvantages. Wet-winding, while offering the advantage of simple oven curing, is not conducive to fiber placement. The versatility of fiber placement is its capability of winding complex shapes using more of a variety of winding angles, changing angles while winding, and cutting and adding tows on demand. Fiber placement, on the other hand, needs high performance prepreg systems, and requires consolidation using a vacuum bag and autoclave pressure 25 during curing. Also, in the fabrication of very thick structures where many layers of fiber are superimposed on each other, waves in the superimposed layers are normally formed because of debulking (i.e., elimination of voids) during curing of the structure in an autoclave.

The present invention overcomes the disadvantages of the prior art by substantially curing the fiber as it is being laid down on the workpiece on the mandrel in a system to be marketed under the trademark 30 "Cure-on-the-Fly".

The present invention is directed to a method of producing substantially cured fiber reinforced laminations in situ while laying up thermoset resin impregnated fiber tow or tape on a mandrel comprising:

- 35 a) passing the at least one thermoset resin impregnated fiber tow or tape to a preheating zone for preheating the thermoset resin impregnated fiber tow or tape to a sufficient temperature so that curing of the thermoset resin is partially advanced, and
- b) laying up the partially advanced, preheated thermoset resin impregnated fiber tow or tape onto the mandrel while simultaneously advancing the curing of said thermoset resin to substantial completion (i.e., greater than 60%) by

- 40 i) supplying heat to the area of the mandrel proximate to where the thermoset resin impregnated fiber tow or tape is being placed thereon,
- ii) monitoring a plurality of parameters characteristic of said fiber placement system or thermoset resin impregnated fiber tow or tape, and
- iii) controlling the amount of advancement of ours of the resin in the thermoset resin impregnated fiber tow or tape as a function of the monitored values.

45 Preferably said monitored values are predetermined.

Preferably, in step a) the preheating is to a predetermined temperature based on the particular thermoset resin in the range of from ambient to about 375°C where the curing of the thermoset resin is partially advanced.

This invention is also directed to a fiber placement system for performing the above mentioned method 50 comprising:

- a) means for preheating the at least one thermoset resin impregnated fiber tow or tape to a sufficient temperature within an advancement to ours range for a sufficient time period based on the resin for partially advancing the resin to cure,
- 55 b) means for laying up the preheated, partially advanced thermoset resin impregnated fiber tow or taps to cure the thermoset resin on a mandrel, and
- c) nip point heating means associated with at least one parameter monitoring means located proximate to the laying up means for simultaneously heating the tow or tape to a temperature within the curing range of the resin while the tows or tape are being placed on the mandrel and the curing of the resin is

being further advanced to substantially completion. Preferably, the sufficient time period and the sufficient temperature are predetermined.

Figure 1 is a side view of one embodiment of the delivery head that has two ribbonizing sections therein for practicing the inventive fiber lamination method.

5 Figure 2 is a side view of another embodiment of the delivery head that has only one ribbonizing section therein for practicing the inventive fiber lamination method.

Figure 3 is a schematic view showing the components of the nip point heating means of the invention.

10 Figure 4 is a perspective view of a complete fiber placement system using the Cure-On-The-Fly system.

This invention uses chemical advancement of thermoset resin systems to achieve a substantial degree of cure during the process of fabricating composite structures. One approach is to advance the prepreg tow material as close to cure as practicable in an off-line process (i.e., a system where the tows or tape is impregnated and advanced to cure independent of the laying up system). A practical limitation to the degree of advancement of the matrix system is that the matrix can not be at greater than 60% crosslink 15 density when the tows or tape (sometimes referred to as "band") is placed on the workpiece on the mandrel as the first layer or as superimposed layers over the first layer: once a layer has another layer superimposed on top of it, the under layer is referred to as "underlayment". The matrix system should also be pliable and conformable to the underlayment. This degree of advancement of the matrix system, in part, depends on the resin content and the physical and chemical characteristics of the resin system. A resin 20 system that achieves a high percentage of chemical conversion at gel (i.e., the term gel denotes the degree of advancement at which the resin transitions from a liquid to a rubbery, or solid state) is more suitable for off-line advancement, while the inherent stiffness of the polymer exercises a limitation on the degree of crosslinking that can be tolerated without compromising manufacturability. When an off-line process is used where the resin in the tows or tape is advanced to near gel by low temperature (such as 100° to 120°F) 25 oven staging, this process requires a resin system that can be advanced to a quasi thermoplastic state of advancement to cure (or gel) without the layers of tow on a spool sticking together or becoming too stiff for unspooling. Longer gel times can be tolerated because of the nature of this off-line process. Substantial further advancement to cure is accomplished by directing a high temperature heat source such as an air torch, on the prepreg tow during winding as it is processed through a nip-point compaction head. This 30 process may optionally be followed by a postcure in an oven or other energy sources.

A second approach is to apply on-line cure staging by passing the prepreg tow through a heated delivery tube, which will bring the matrix system to between 40 and 60% crosslink density during the fabrication of a composite part. The underlays can be, and usually are greater than 60% crosslinked. The resin characteristics desired for this approach are: latency of gelation (or curing) at subambient 35 temperature and short gel times at elevated temperatures and flexibility and spreadability at process temperatures; the resin matrix also must be able to form a cohesive bond between the underlayment and overlayer.

The resin matrices used in the invention for impregnating fibrous tows, unidirectional (in a single direction on the workpiece) and/or crossply (crisscross direction) tapes are thermoset resins. Non-limiting 40 examples of thermoset resins that can be used in this invention are epoxy, phenols, cyanate esters, bismaleimides type resins, and mixtures thereof. The temperature at which the resin cures depend upon the type resin being used.

The in-situ consolidation and void removal steps used in practicing the instant invention will depend on the prepreg system being used. The initial advancement of the prepreg tow is achieved by passing it 45 through a high temperature (e.g., 300° to 500°F) heating zone on the fiber placement machine, in an on line (or in-situ) process. Short gel times are required for the resin system because of the speed at which the resin must gel. The conformability required for part fabrication is achieved by maintaining the prepreg tow at high temperatures with nip point heating as it is advanced, thereby, facilitating delivery of the prepreg tow. The advanced material is passed through a nip point compacting delivery head, at which point 50 additional heat (e.g., at a temperature 300 to 800°F) is applied and the material becomes substantially cured (that is greater than 60% cured). The resulting part can be fully cured using several different energy sources without the use of additional consolidation steps, i.e., vacuum bags or autoclaves.

Generally, the underlays, when they are laid down, have a crosslink density of equal to or greater than 40%, preferably greater than 60%, while it is desirable that the overlays to be laid down should have a 55 crosslink density in the range of 40-60%. This is desirable so that the interfacing surfaces of adjacent layers will crosslink together forming a homogeneous (continuous), workpiece without forming seams. In other words, it is desirable that the individual layers cannot be recognized in a cross sectional view of the workpiece but rather that it appears to be uniform. After the fibrous material has been laid down to become

EP 0 534 092 A1

underlayers, these underlayers will continue to be crosslinked from the heat of the nip point heating of the overlayer being laid down until the underlayer is completely insulated from the heat of the overlayer. This insulation will occur after a certain number of layers are laid down on top of it depending upon the thickness of the layers being overlaid (i.e., it may occur after as little as two superimposed layers or it might take 5 many layers such as from 3 to 10 or higher). Hence, the underlayers can be crosslinked to a greater than 75% crosslink density, preferably greater than 95% crosslink density, because of the continuous heat effect of the nip point heating of the overlays.

In an example of how models are developed for the temperature/time profiles for programming the on-line operation unit of the fiber placement system for achieving the desired percentage of crosslink density 10 for the underlayers and overlays, the following experimental procedure was conducted on three different epoxy type resins for such determinations. The resin systems used in these experiments are resins of Hercules Incorporated as follows:

- 15 1) resin A - is a hotmelt, 250° F curable epoxy resin system developed to operate at temperatures up to about 180° F.
- 2) resin B - is an amine-cured epoxy resin system for general purpose structural applications in temperature environments up to 275° F.
- 3) resin C - is an amine-cured, toughened epoxy resin system developed as a low-flow system to operate in temperature environments of 250° F. The impact and damage tolerance properties of resin C are superior to those of other structural epoxy resin systems.

20 Instantaneous gel tests were run on a Fisher Johns hot stage, where the temperature was controlled to $\pm 1^{\circ}$ F. A small amount of resin was placed on the temperature stabilized hot stage and the timer was started. When the resin reached a state where it no longer flowed together, i.e., gelled, the timer was stopped. After the gel had been determined at several temperatures, a graph was developed on semilog graph paper. The time and temperatures measurements for the graphs were as follows:

25 1) For resin A:

	TIME (sec)	TEMPERATURE (° F)
30	424	250
	196	275
	55	317
	50	326
	20	373
	20	369
35	13	417 (started to show degradation)

2) For resin B:

	TIME (sec.)	TEMPERATURE (° F)
40	300	350
	35	417
	30	424
45	15	450
	12	451
	5	490
	4	496
	3	502 (started to show degradation)

50 3) For resin C:

TIME (min.)	TEMPERATURE (° F)
80	225
55	250
27	300
12	350
7.5	375
3.3	425
1.4	475
1.2	500

5
10

Based on the above mentioned measurements, the truest line was drawn on semilog graph paper and the line was extrapolated from 325° to 550° F; this line represented a 100% gel of the resin system. From this experimental line, the percentage of crosslink was estimated in order to obtain the preferred range of 40 to 60% crosslink density lines for each resin and these estimations were plotted on semilog paper using the same slope as the experimental data provided; these plots were used as the "process window". In order to use this process window for setting up the parameters of the fiber placement system, the total transient time in the heating section of the particular fiber placement head had to be considered. Using this transient time, the average heating temperature was derived for use in the process in order to obtain a given level of conversion.

15
20
25

For completion of a closed loop control, the temperature at the outlet of the air gun used for supplying the nip point heating was also monitored. The mandrel rotation of the fiber placement system was controlled at a predeterminate speed; and the means for monitoring a plurality of parameters includes means for monitoring the speed of the mandrel. A monitor and keyboard are linked to the operating computer of the fiber placement system for enabling operator input and control of the system.

30
35
40
45

For a more detailed description of the invention, Figures 1 and 2 illustrate preferred embodiments of the invention. Creel fed partially advanced or nonadvanced prepreg tows 10 that are composed of a high temperature resistant, high performance thermoset resin (such as an epoxy resin) having continuous fibers are continually fed into apparatus 1 where a plurality of prepreg tows 10 (i.e., up to five tows in each of upper and lower paths) enter into the preheating zone 2 through vertically and horizontally situated guide rollers 17 and 18 where half of the tows enter in upper and lower parallel paths; this preheating zone has heating means 3 that heats the tows or tape to a temperature range of 300 to 500° F for partially advancing to cure the fiber. Perforated plates 19 separate the upper and lower paths and evenly distributes the heating gases from heating means 3. Tows 10 are then passed through distribution means which is in the form of comb 4; then the tows are guided through first ribbonizing section 5. In the upper and lower ribbonizing sections 5 the tows are shaped into the desired shape, such as flattened individual tows or as a consolidated band. The individual tows or tape is then guided onto a wedge shaped platform where the tows or tapes meet in a single plane immediately before passing into an optional second ribbonizing compaction section 6 where the tows or tapes are formed into single band (Figure 1). Although Figures 1 and 2 show embodiments that has ribbonizing sections therein, a ribbonizing section is only optional and not required in other embodiments not shown; this is especially true where tapes are preformed before entering the fiber placement system of this invention for laying down. It should also be noted that the ribbonizing section can be an independent device attached to the system for use therewith. This band then passes to roller 19 and is pressed onto mandrel 22 not shown. At the point where the tows or tape is placed onto the workpiece on the mandrel 22, heating means 7 heats the tows or tape to a higher temperature above 500° F simultaneously as it is being placed on the mandrel to substantially completely cure the resin therein (that is, to cure the resin to greater than 60%).

50

As depicted schematically in Figure 3, air flow through the heater 7 is controlled by the air flow and controlled device 8. The temperature is maintained by varying the amount of power with the power control and regulating system 9. The resin impregnated fiber is to be heated to a temperature no greater than the melt temperature of the matrix resin. This nip point heating is extremely fast (that is, 1 to 2 seconds).

55

Closed loop control is achieved by monitoring the temperature of the composite on the mandrel 22 with infrared temperature censor 15. The temperature, along with fiber speed, as determined by tachometer 16, is processed by controlled computer 10. In addition to the above-mentioned parameters of fiber temperature and speed, the computer determines the amount of air flow and air temperature which is required by assessing requirements of the process as input from the main fiber placement machine controlled computer 11.

Additional control is achieved by modeling the effect of heat on the composite resin. Excessive heat can cause areas of localized degradation in extreme cases, and an exothermic reaction can result. Conversely, insufficient heat to the fiber would not supply the required advancement to cure tackiness or compliance required to make a good article. During fiber placement on irregularly shaped mandrels, it is known to vary 5 the speed of fiber placement, depending upon the particular application location of fiber placement on the mandrel. For example, the speed of fiber placement can be decreased as somewhat intricate turn or edges are traversed by the fiber delivery head. As the temperature of the composite is a function of the difference in temperature between the air source and fiber being heated, as well as the length of time the temperature is applied, modeling is necessary to keep fiber temperature within required limits as the speed of the fiber 10 varies.

The amount of heat applied in the nip point heating can be controlled by controlling the preheat section 2 of the invention via a computer model, as a function of the shape of the mandrel, e.g., and as a function of the composition of the fiber tow being laid. The temperature of the heated air and the quantity of air per unit of time produced at the air gun 7 can be selectively increased or decreased and/or the duration of the 15 heated air, e.g., can be selectively controlled throughout the laying of fiber upon the mandrel during the formation of the article.

Redundant regulation of the system is accomplished by monitoring the temperature of the air leaving the heater with a thermal couple 12. Should the temperature rise too high for too long, as predetermined by operator experience, the process will be interrupted by a separate safety monitoring system 14. Operator 20 input and control are accomplished through a monitor and keyboard 13.

Figure 4 illustrates, in perspective, a filament placement system 20 in which the Cure-on-the-Fly™ system of the present invention can be used. Individual rovings or tows 10 are passed from the creel 21 to the delivery head 1, which is mounted onto a manipulator, and emerge at the delivery, or compaction, roller 19 (shown in Figures 1, 2 and 3). The compaction roller 19 applies the tows 10, formed into a band, onto 25 the rotating mandrel 22. The air heater 7 is shown in Figure 2 as being attached to the delivery head 1, but, if desired, can be a free standing, movable device or can be attached to another part of the fiber placement system where practicality dictates for the most efficient operation. Operation of the fiber placement machine 20, including the delivery head 1, is controlled by computer 11 (shown in Figure 3).

The articles manufactured by the process of the instant invention are a high fiber volume, low void 30 content, composite part which can be fully cured (i.e., to a 100%) using several different energy sources without the aid of additional compaction steps such as vacuum bags or autoclaves. This process will allow large structures to be fabricated more efficiently without the use of ovens or autoclaves. Extremely thick structures can be fabricated without wave formation, due to debulking during curing. Possible exotherms 35 can be reduced because of the lower energy potential of the matrix system going into the final cure. Given the appropriate resin system, this process will allow for total cure of the composite at the time of fiber placement.

Claims

- 40 1. A method of producing a substantially cured fiber reinforced lamination in a fiber placement system in situ while laying up thermoset resin impregnated fiber tow or tape on a mandrel comprising:
 - a) passing the at least one thermoset resin impregnated fiber tow or tape through a preheating zone for preheating the thermoset resin impregnated fiber tow or tape to a sufficient temperature so that the curing of the thermoset resin is partially advanced, and
 - 45 b) laying up the partially advanced, preheated thermoset resin impregnated fiber tow or tape onto the mandrel while simultaneously advancing the curing of said thermoset resin to substantial completion of greater than 60% crosslink density by
 - i) supplying heat to the area of the mandrel proximate to where the thermoset resin impregnated fiber tow or tape is being placed thereon,
 - 50 ii) monitoring a plurality of parameters characteristic of said fiber placement system or thermoset resin impregnated fiber tow or tape, and
 - iii) controlling the amount of advancement of cure of the resin in the thermoset resin impregnated fiber tow or tape as a function of the monitored values.
- 55 2. The method of claim 1 wherein the partially advanced, preheated thermoset resin impregnated tow or tape are passed to a ribbonizing zone for shaping into the desired shape prior to being laid down.

EP 0 534 092 A1

3. The method of any of the preceding claims wherein the laying up comprises passing the partially advanced thermoset resin impregnated fiber tow or tape at a delivery or compaction roller.
4. The method of any of the preceding claims wherein the step of monitoring a plurality of parameters comprises monitoring a temperature of said area being heated in the step c) i).
5. The method of claim 4 wherein said step of monitoring a temperature comprises monitoring a temperature by means of an infra red temperature sensor.
10. 6. The method of any of claims 1-4 wherein said step of supplying heat is performed by an air gun.
7. The method of claim 6 wherein the step of monitoring the plurality of parameters comprises monitoring a temperature at an outlet of said air gun.
15. 8. The method of any of claims 6 or 7 wherein the step of controlling an amount of heat supplied by said means for supplying heat further comprises the step for terminating heat supplied to said area in the event that said heat supplied reaches a temperature above a predetermined value.
9. The method of any of the preceding claims wherein the mandrel is adapted to rotate at a predetermined speed, and the step of monitoring a plurality of parameters comprises monitoring the speed of said mandrel.
20. 10. The method of any of the preceding claims wherein said step of supplying heat is performed by an air gun and controlling the amount of heat supplied in said step of supplying heat comprises controlling the temperature and air flow rate.
25. 11. The method of any of the preceding claims wherein said step of controlling the amount of advancement of cure of the resin is a function of composition of said thermoset resin impregnated fiber tow or tape.
30. 12. The method of claim 11 wherein the resin has a predetermined melt temperature, and the step of controlling the advancement of cure of the resin comprises maintaining said amount of heat at a temperature below the melt temperature of said resin.
35. 13. The method of any of the preceding claims wherein the method further comprises impregnating at least one fibertow or tape with at least one thermoset resin.
40. 14. The method of any of the preceding claims wherein in said step a) the thermoset resin impregnated fiber tow or tape to a predetermined temperature based on the particular thermoset resin in the range of from ambient to about 375 °C where the curing of the resin is partially advanced and the monitored values are predetermined.
45. 15. A fiber placement system for producing cured fiber reinforced lamination in situ while laying up thermoset resin impregnated fiber tow or tape on a mandrel comprising:
 - a) means for preheating the at least one thermoset resin impregnated fiber tow or tape to a sufficient temperature within an advancement to cure range for a sufficient time period based on the resin for partially advancing the resin to cure,
 50. b) means for laying up the preheated, partially advanced thermoset resin imprgnated fiber tow or tape to cure the thermoset resin on a mandrel, and
 - c) nip point heating means associated with at least one parameter monitoring means located proximate to the laying up means for simultaneously heating the tow or tape to a temperature within the curing range of the resin while the tows or tape are being placed on the mandrel and the curing of said at least one thermoset resin is being further advanced to substantially completion.
55. 16. The fiber placement system of claim 15 wherein ribbonizing means for shaping the tows into a desired shape is included in the system prior to the means for laying up.
17. The fiber placement system of any of claims 15 or 16 further comprising means for impregnating at least one fiber tow or tape with a thermoset resin.

EP 0 534 092 A1

18. The fiber placement system of any of claims 15, 16 or 17 further comprising a delivery or compaction roller for laying up the at least one partially cured thermoset resin impregnated fiber tow or tape onto the mandrel.
- 5 19. The fiber placement system of any of claims 14, 15, 16, 17 or 18 wherein the sufficient time period and sufficient temperature are predetermined.

10

15

20

25

30

35

40

45

50

55

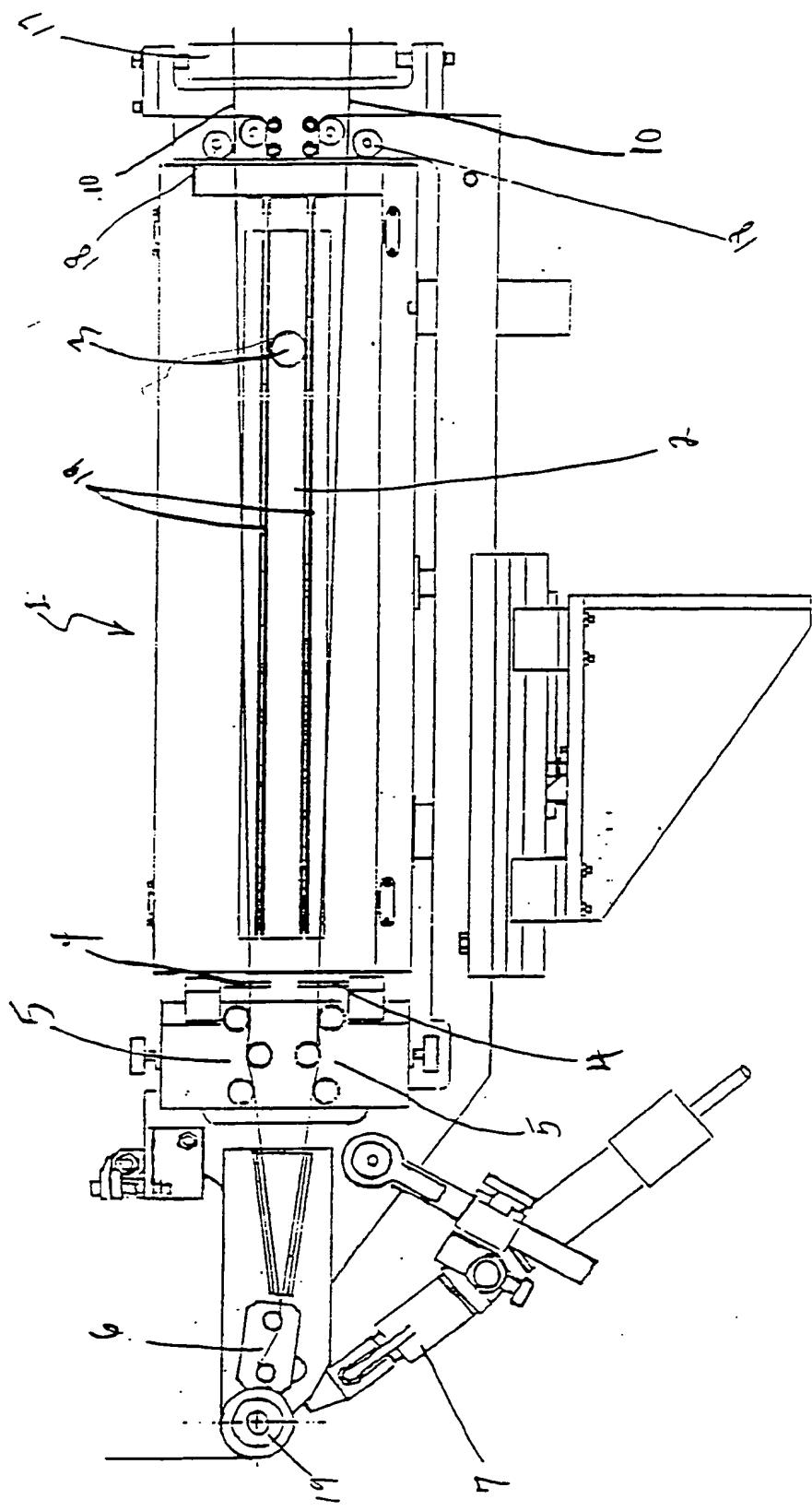


FIGURE 1

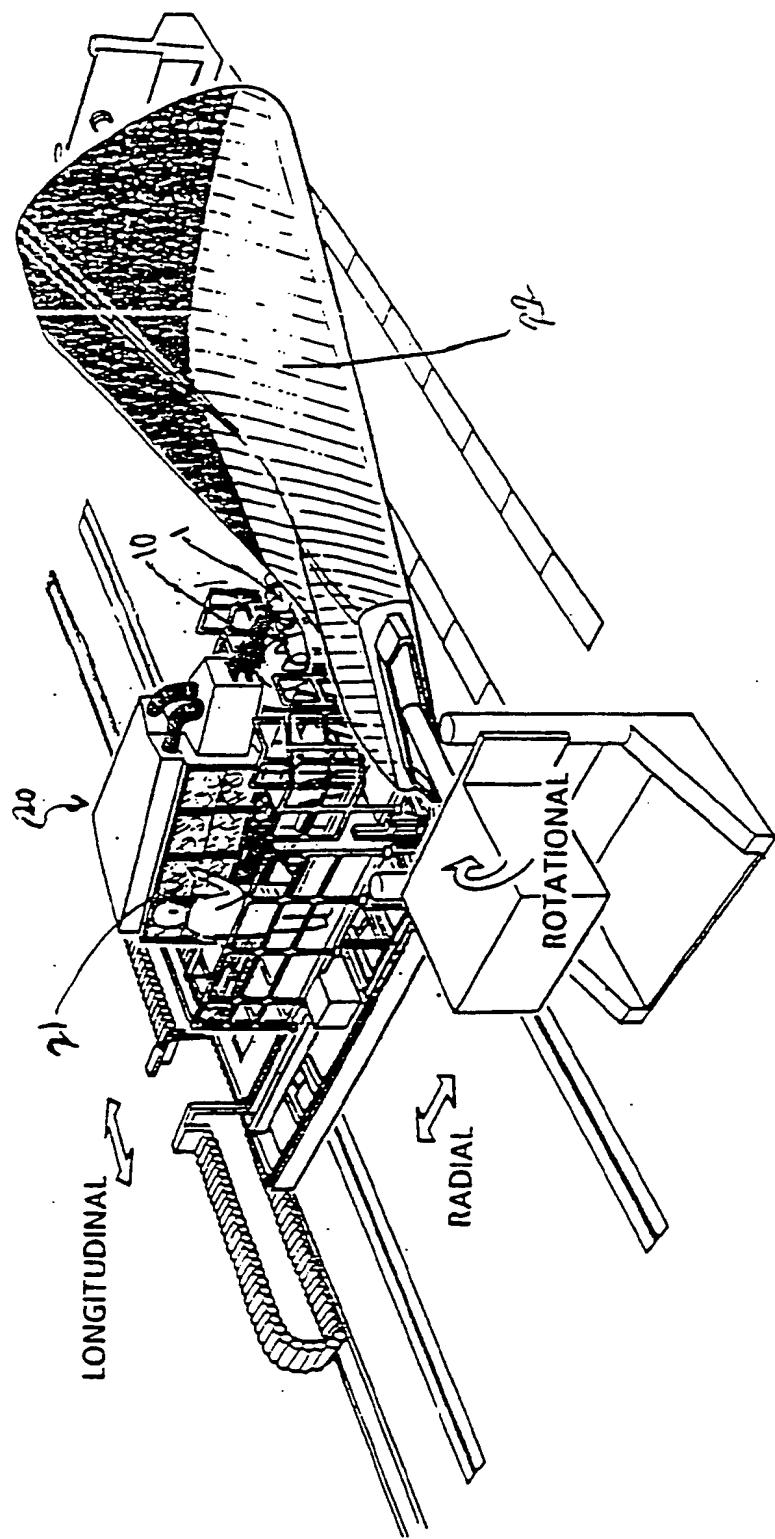


FIGURE 4



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 2943

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WO-A-8 400 351 (BOEING) * page 7, paragraph 2; claims 11,24,25 * ---	1-19	B29C67/14 B29B15/08
X	WO-A-9 007 428 (ZSOLNAY) * page 36, line 22 - page 37, line 10 *	15-19	
A	---	1-3	
A	US-A-3 574 040 (CHITWOOD ET AL.) * column 4, line 1 - line 16 *	1-19	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B29C
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	30 OCTOBER 1992	VAN WALLENE A.M.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : intermediate document	A : member of the same patent family, corresponding document		